Automated water determination in chocolate

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Karl Fischer

Summary

For a variety of reasons, the water content of chocolate is of crucial importance and has to be accurately determined. This poster compares an automated version of the Karl Fischer titration (KFT) using the sequential addition of various solvents with the widespread manual titration at elevated temperatures using a chloroform/methanol mixture. The water contents determined by the two procedures show excellent agreement. However, manual titration requires labor-intensive sample preparation, the side reactions are difficult to quantify and hazardous halogenated solvents have to be used. In contrast, automated KFT is straightforward, uses non-hazardous solvents, allows to quantify the side reactions and is easily applicable to water determinations in sugar- and fat-containing matrices.

Introduction

The water content in chocolate determines to a large extent the taste and the chemical, physical, microbial and shelf-life properties of the product. Especially for the processing of the chocolate bar, the quantitation of the water content is of crucial importance, since it determines the flow characteristics of the chocolate mass. Accordingly, straightforward and accurate methods for water determination are required. The method of choice is Karl Fischer titration (KFT) using state-of-the-art technology.

Chocolate essentially consists of cocoa liquor, cocoa butter, milk powder and sugar in various concentrations and does not form solutions or stable suspensions with methanol or other Karl Fischer solvents. The fatty ingredients such as cocoa butter and cocoa liquor need a lipophilic solubilizer to become soluble, whereas the polar components such as sugars need hydrophilic solvents. KF titration, however, still requires methanol or a KF solvent. Mixtures of lipophilic and hydrophilic solvents would cancel each other out and nothing would be gained.

Previous methods using a volumetric stand-alone titrator suggest using titration at elevated temperatures (50 °C) to dissolve the fatty compounds. This procedure is labor-intensive, cannot be automated and requires large quantities of hazardous halogenated hydrocarbons. These drawbacks can be overcome by the sequential addition of various solvents. In the first step white spirit is added to approximately 0.5…1 g of the chopped-up chocolate sample. Within one minute the fatty compounds are dissolved. After this, formamide is added to dissolve the hydrophilic compounds. Finally, the KF working medium is added.

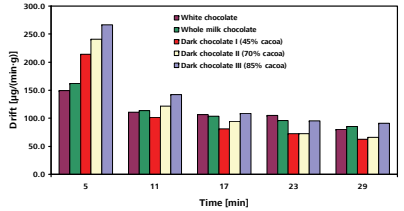
The distinctive feature of this technique consists in the use of white spirit, a halogen-free solvent mixture made up of aliphatic and alicyclic hydrocarbons that is not hazardous to the environment and that does not form a homogeneous mixture with the other solvents, but instead remains as a second phase. The procedure can be fully automated using a sample changer and a titrator.

System setup

- 841 Titrando (volumetric KF titrator)
- 814 USB Sample Processor
- 800 Dosino
- 802 Stirrer (not shown)

The preliminary titrations showed markedly delayed endpoint detection. After titration of the released moisture, reagent consumption continued, indicating a retarded water release from the sparingly soluble cellular cocoa matrix or iodine-consuming side reactions. Since the removal of the cellular matrix had no effect on the titrant consumption, the first hypothesis could be ruled out. In contrast, some dissolved cocoa ingredients must have reacted with the iodine simulating the presence of water. After titration of the released water, continuous titrant additions, evaluated at defined time intervals, allowed reliable estimates of the extent of the side reactions.

Side reactions



Manual moisture determination

KFT is based on the stoichiometric reaction of water with iodine and sulfur dioxide in the presence of a short-chain alcohol (R` = CH_3, C_2H_5) and an organic base (RN), according to the following equations:

$$R`OH + SO_2 + RN \rightarrow R`OSO_2^- + RNH^+$$

$$R`OSO_2^- + I_2 + H_2O + 2\,RN \rightarrow 2\,RNH^+ + R`OSO_3^- + 2\,I^-$$

$$R`OH + SO_2 + 3\,RN + I_2 + H_2O \rightarrow 3\,RNH^+ + R`OSO_3^- + 2\,I^-$$

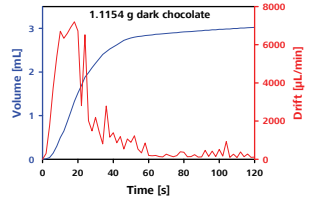
A prerequisite for KFT is that the water in the sample is freely available for titration. After thorough trituration, the chocolate sample is added to the sealed thermostatted titration vessel containing a 1:1 mixture (volume/volume) of HYDRANAL®-Solvent and chloroform. Titration of the released water is performed at 50 °C with HYDRANAL®-Titrant 2. While titration at higher temperatures significantly improves water release, side reactions become more pronounced. Besides the problem to correct for these reactions, the use of climate-affecting and potentially carcinogenic chlorinated solvents is a major drawback.

Repeatability

	Dark chocolate I (45% cocoa)										Mean value	RSD
	1	2	3	4	5	6	7	8	9	10	[%]	[%]
Sample weight [g]	0.6902	0.6432	0.6050	0.7746	0.6073	0.8898	0.3562	1.2539	0.7884	0.7939		
Water content [%]	0.98	1.00	0.97	0.99	0.94	0.98	0.96	0.92	0.93	0.93	**0.96**	**2.73**

Automated moisture determination

- Initially, the Dosinos are pre-flushed to prepare the system
- Three «blank determinations» (working medium without sample) are carried out
- The titer of the titrant is determined with the commercially available water standard (n = 3)
- A defined amount of triturated chocolate (0.5…1.5 g) is directly weighed out into the 75-mL sample vessel
- All sample vessels are sealed with aluminum foil and a foil holder
- Samples are placed on the sample processor rack and all relevant data (sample weight, sample identification) is entered into the ***tiamo***™ software
- 14 mL of white spirit is transferred to the sample vessel
- After stirring for 60 s, 10 mL formamide is added
- After stirring for another 60 s, 12 mL of HYDRANAL®-Methanol Rapid is added
- After the titration of the released water with KF reagent, the side-reaction-induced drift is determined



Comparison

		Manual titration	Automated titration
Chocolate sample weight [g]	**cocoa-free**	0.5-1.0	1.0
	low cocoa content	1.0-1.5	
Titrant		HYDRANAL®-Titrant 2[a]	HYDRANAL®-Composite 5[a]
Working medium		15 mL chloroform[a] 15 mL HYDRANAL®-Solvent[a]	14 mL petroleum[a] 10 mL formamide[a] 12 mL HYDRANAL®-Methanol Rapid[a]
Temperature of the working medium [°C]		50	25
Determination time [s]		360	360
Solubility of hydrophilic ingredients		rather poor	excellent
Water release from sugars and proteins		extraction at higher T	solubilization
Stop time [s]		300	120
Side reaction correction		impossible	possible

[a]all chemical products were kindly provided by Sigma-Aldrich Laborchemikalien, Seelze, Germany.

Sample		Manual titration No[a]	Water content [%]	RSD [%]	Automated titration No[a]	Water content [%] No side reaction correction	Water content [%] Side reaction correction	RSD [%]
White chocolate		3	**0.77**	**8.20**	4	0.84	**0.78**	**2.44**
Whole milk chocolate		2	**0.88**	**2.81**	4	0.94	**0.88**	**4.57**
Dark chocolate	**I (45% cocoa)**	10	**0.96**	**2.73**	10	0.99	**0.93**	**2.49**
	II (70% cocoa)	2	**0.82**	**7.11**	4	0.90	**0.79**	**2.61**
	III (85% cocoa)	3	**1.06**	**0.67**	4	1.17	**1.06**	**3.75**

[a]number of determinations

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